Investigation of AgAlCuZr Amorphous / Crystalline Structure Produced by Casting and Milling

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Abstract: Advanced $Ag_8Al_8Cu_{36}Zr_{48}$ master alloys were produced by arc- and induction melting and examined. The arc-melted ingot has an amorphous structure with a certain amount of metastable phase, compared to the induction-melted ingot, which contained $AlCu_2Zr$, $CuZr_2$ and Ag_3Al phases. Amorphous wedge-shape samples were produced by centrifugal casting from the arc-melted master alloy. Amorphous/crystalline powders were synthesized by ball-milling with different milling times from the induction-melted master alloy. The resulting powder contained Ag_2Al phase after 5h milling, the amount of which was reduced after 9h milling. The thermal stability of the samples was investigated by DSC. The effective activation energies of the first crystallization were evaluated according to Kissinger's method and there were found to be the same, 271-268 J/g. The low activation energy suggests a good ductility.

1. Introduction

Bulk metallic glasses (BMGs) have been developed in the last decades because of their unique mechanical, chemical and magnetic properties [1-3]. These glassy alloys are generally brittle depending on their composition because they have low atomic mobility. In order to reach a wide application of these BMG's, it is necessary to increase the ductility by generating multiple shear bands and preventing sudden destructive processes [4]. The brittleness of the amorphous structure disappears and the sample becomes ductile owing to the alloying elements with positive heat of mixing and the ductility of the formed crystalline parts. Ag and Al combined with Cu and Zr can be a good association to obtain a ductile and tough BMG. The ductility can be enhanced by nanosized crystalline parts formed by partial crystallization of BMG's, which can prevent the development of cracks and improve the ductility of the material [4]. The crystalline parts can be formed from the amorphous structure (produced by annealing) or from the crystalline phases remaining from the initial material (in the case of ball-milling).

Glassy alloys can be produced by quenching [1, 3] and by solid state techniques such as mechanical milling or alloying [2, 3]. Amorphous alloys can be produced by rapid cooling to the glass temperature in order to avoid the gem forming. Depending on the cooling rate, amorphous alloys with various properties can be produced. The other common method to produce amorphous alloys is the milling, especially the ball-milling. During milling, the effect of the transmitted energy causes the formation of the amorphous structure in the powders.

Accordingly, in this work $Ag_8Al_8Cu_{36}Zr_{48}$ master alloys were produced by induction and arc-melting, the amorphous/crystalline structure was subsequently produced by casting and ball-milling. A small amount with high quality and purity of master alloy can be produced by the arc-melting. A high quality master alloy is required to produce amorphous alloy by casting. A larger, but not homogenous ingot can be produced by induction melting. This initial alloy can be used to produce an amorphous/nanocrystalline powder by milling. The structure, amorphous fraction and thermal properties of samples prepared by different techniques were compared.

2. Experimental procedures

Master alloy ingots were prepared by arc melting and induction melting by mixing pure metals under purified argon atmosphere. Wedge-shaped samples with dimensions 30 mm x 3 mm x 20 mm were produced by centrifugal casting in copper die under argon atmosphere from the arc-melted master alloy. The cooling rate was about 1300 K/min at the base, while it exceeded the 20.000 K/min at the tip, which was determined in Ref. 5. The induction melted master alloys were grinded and fractioned to particle size below 320 μm for the ball-milling. The mechanical milling was performed in a Pulverisette 5 high energy ball-mill in argon atmosphere using stainless steel vial and balls with a diameter of 5, 7 and 10 mm [6]. The overall process lasted 9 h.

The structure of the ingots and powders was confirmed by 1830 I Amray and Zeiss EVO MA equipped with an EDX DX4 and LS Series Scanning Electron Microscopes and a Bruker D8 Advance X-ray diffractometer (XRD) using Co Kα radiation ($\lambda = 0.179024$ nm). The amorphous rate of the powder was measured by Quantimet Image Analyzer using Leica Software. The thermal analysis was performed by a Netzsch 204 Differential Scanning Calorimeter (DSC) at the heating rate of 40 °C/min. To create the Kissinger plot, DSC measurement was performed at heating rates of 5-60 °C/min under Ar atmosphere with a relative error of measurement less than ±1%. The microhardness was measured by a Reichert Vickers tester using a load of 100 g for 15 s.

3. Result and discussion

3.1 Analysis of the master alloy ingots

In accordance with the respective cooling rates and the producing conditions, the master alloys of identical composition displayed two different states. The master alloy produced by arc melting cooled down more rapidly. The surface of the sample being in contact with the Ar atmosphere during arc melting cooled at a minimum rate of 100 K/s. The cooling rate of the bottom surface of the samples being in contact with the inner surface of the copper die was considerably higher. The master alloys prepared by induction melting cooled more slowly.

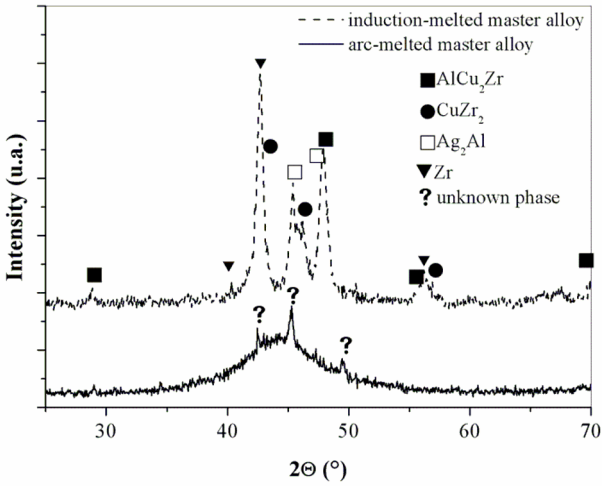

Fig. 1 XRD patterns of the master alloy ingots

It can be seen in Fig. 1 that the XRD pattern of the master alloy produced by arc melting consists of only a number of broad peaks and a diffuse halo indicating that the master alloy has an almost glassy structure. This is due to the cooling rate of the master alloy ingot being enough to suppress the nucleation. The formed phases were metastable phases, which were not be found in the available XRD database.

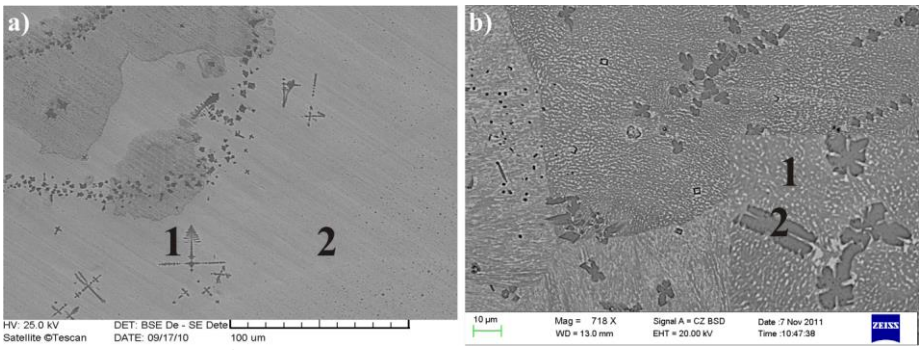

Fig. 2 Microstructure of the ingots a) Arc-melted master alloy ingot b) Induction melted master alloy

Observing Fig. 2a), these were confirmed, being the phases with the size of 10-30 nm (signed as point 1) solidified in the amorphous matrix (signed as point 2). The alloy was homogenous, because the ingot was remelted four times in order to ensure chemical homogeneity. Ingots in larger quantities were produced by induction-melting, which was required to the milling because of the size of the jar. However, the induction melted master alloy has a full crystalline structure due to the slow cooling rate. $AlCu_2Zr$, $CuZr_2$ and Ag_3Al phases were identified by XRD (Fig. 1). TEM analysis is under process. It is necessary to mention, that pure Zr was found as well. Since all amount of the ingot was grinded and put into the jar, the pure Zr could have been mechanically alloyed during the milling. Fig. 2b) presents the structure of the induction melted ingot. The phase signed as point 2 corresponded to the $AlCu_2Zr$ phase measured by EDS and point 1 was an eutectic structure with $CuZr_2$ and Ag_3Al phases.

3.2. Analysis of the wedge-shape sample

Observing the XRD pattern and SEM micrograph of the cross-section of the wedge-shaped sample shown in Fig. 3a) and b), it is evident that it had a fully amorphous structure.

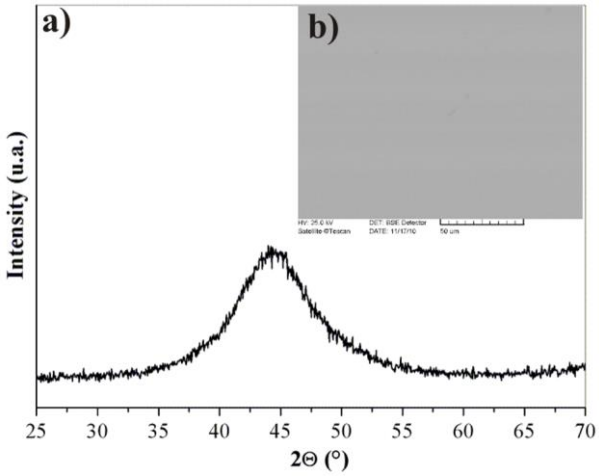

Fig. 3 Analysis of the of the wedge-shaped cast sample a) by XRD b) by SEM

This sample showed a microhardness of 458 MHV/100 g. Based on the thermodynamic examination, each amorphous wedge-shape sample expressly exhibited the glass transition, followed by a supercooled liquid region and then by an exothermic reaction due to crystallization (Fig. 4a)).

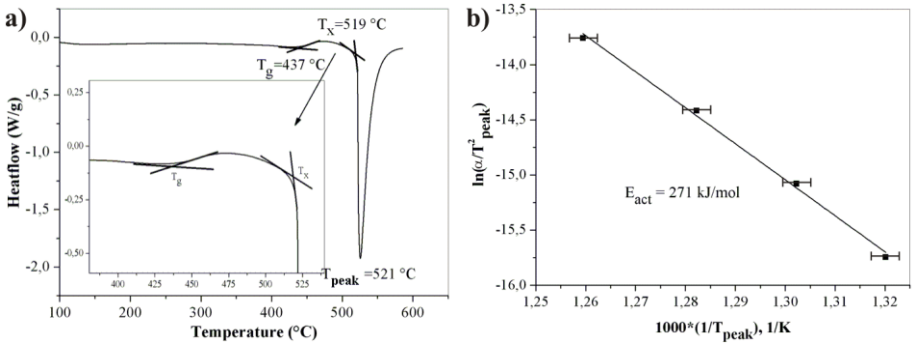

Fig. 4 a) DSC curve b) Kissinger's plot of the first crystallization peak of the wedge-shape sample

The glass transition temperature is at 437 °C, the onset of crystallization temperature is at 519 °C, and the peak temperature of the crystallization is 521 °C. The supercooled liquid region is 80 °C being a wide region. An amorphous structure with low activation energy of crystallization results in positions of the atoms being easily changed by deformation, which leads to the increase of the ductility. The activation energy corresponding to the first crystallization peak was determined using Kissinger's analysis [7]. The activation energy of the first crystallization peak of the cast sample is 271 kJ/mol (Fig. 4b)), which is smaller than published in the literature [8] of 354 kJ/mol for $Ag_7Al_7Cu_{43}Zr_{43}$. This parameter characterises the activity of the atoms, furthermore the plasticity of the alloy, which is excellent for $Ag_8Al_8Cu_{36}Zr_{48}$ metallic glass alloy.

3.3 Analysis of the milled powder

In the case of milled powders, the background in XRD is generally higher than in the case of cast samples. The height and the area of the peaks belonging to crystalline phases decrease with increasing the milling time (Fig. 5a)). Comparing the composition of the crystalline phases to the initial material, there was Ag_2Al phase and no pure Zr was identified after 5h milling.

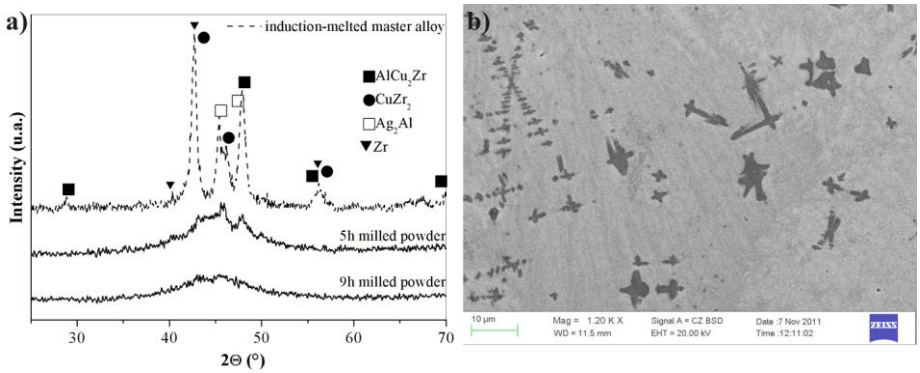

Fig. 5 Analysis of the of the powders a) by XRD after different milling time b) by SEM after 9h milling

The XRD pattern of the milled powder shows that the 9 h milled powder is approximately regarded as amorphous structure (~ 98%), which was confirmed by image analysis, where ~5% of crystalline volume was detected. Fig. 5b) shows the backscattered images of a such particle. This sample has the microhardness of 405 MHV/100 g. As can be seen from the DSC curve of the powder after milling for 9 h, an exothermic peak appears, while the glass transition temperature is not visible (Fig. 6a)).

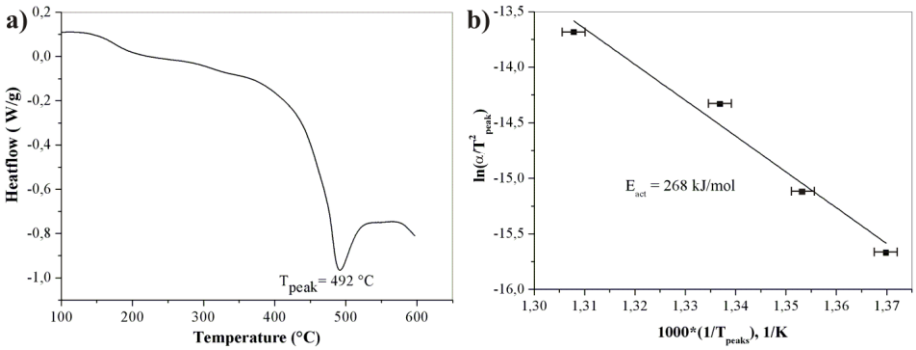

Fig. 6 a) DSC curve and b) Kissinger's plot of the powder after milling for 9 h

It is difficult to analyze the thermal properties of the powder because of their high specific surface. The activation energy of this powder is 268 kJ/mol (Fig. 6b)). This means that there is no difference between the activation energies of the first crystallization peak of the cast sample and the milled powder.

3.4 The influence of relaxation on the properties of the wedge-shape sample and the milling powder

The amorphous state is an instable energy state. Annealing the structure below Tg leads to structural relaxation and a number of physical properties change, such as atomic diffusivity, viscosity or ductility. There is an especially important process in the case of powders. The same initial state was used to carry out the annealing. The wedge-shaped and the powder samples contained ~5 v% of crystalline phases. The wedge-shaped sample and the powder milled for 9 h were relaxed at 300°C for 1 hour. The position of the peak temperature did not change due to the relaxation (Fig. 7) in the case of the cast sample. The glass temperature appeared more pronounced after the relaxation and shifts towards lower values. The enthalpy of first crystallization was 72.83 J/g for the cast sample and 72.3 J/g for the relaxed sample.

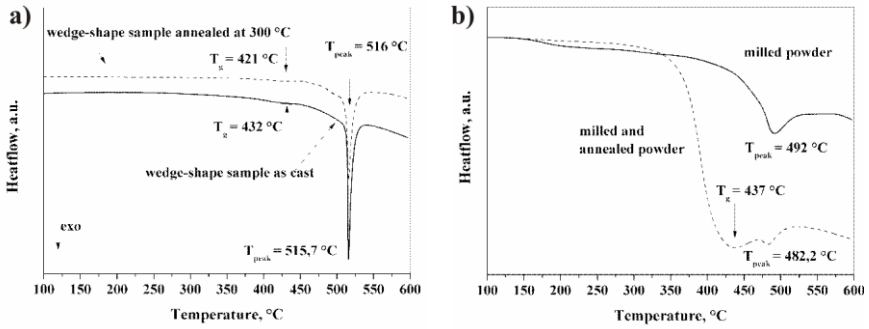

Fig. 7 DSC heating curves of annealed samples a) cast b) milled

The situation is different regarding the milled powder. The peak position of the first crystallization process shifts towards lower values (Fig. 7). The glass temperature becomes visible after the relaxation and it is higher than that in the case of the wedge-shaped sample. The enthalpy of first crystallization of the powder is 2.5 J/g, which is much smaller than the enthalpy of the cast sample. This phenomenon can be caused by the differences between the amorphous structures of the samples produced by the different techniques. There are no changes in the microstructure of the relaxed samples.

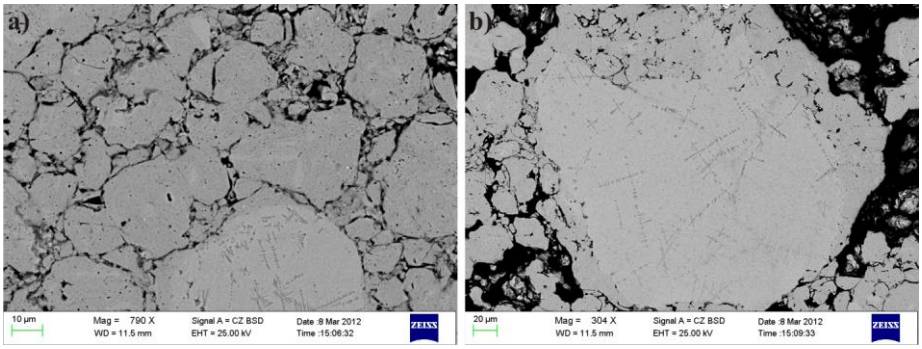

Fig. 8 SEM images of the milled and relaxed powder

Fig. 8 shows SEM images of the relaxed powder. It can be seen that the crystalline phases presented mainly in the particles with the diameter of ~300 µm, which is the maximum size of the starting powder before milling process.

Conclusions

$Ag_8Al_8Cu_{36}Zr_{48}$ bulk amorphous alloy could easily be produced in the size of 3 mm by arc-melting combined with centrifugal casting. Using milling, powder with ~95 v% amorphous amount was produced. A large amount of the powder was amorphous, but the particles with the diameter of ~300 µm of Ag_2Al crystalline phases were present. Sieving the particles below the diameter of ~300 µm, the residual powder had an amorphous structure. The glass transition temperature of the two samples was approximately the same, but the Tg of the powder appeared only after the relaxing. The peak temperature of the first crystallization process was different; the peak temperature of the cast samples is higher than that of the milled powder. The difference was 18°C. The activation energies of the first crystallization process were the same, being 271-268 J/g. The low activation energy indicates a good ductility. The plasticity of $Ag_8Al_8Cu_{36}Zr_{48}$ amorphous alloy was higher than that of any alloy containing Ag-Al-Cu-Zr published in the literature. The microhardness of the samples was 458 HV (cast sample) and 405 HV (milled powder).

Acknowledgement

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